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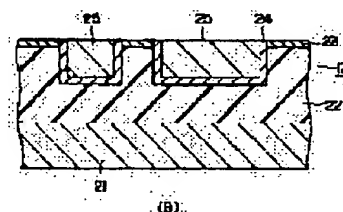
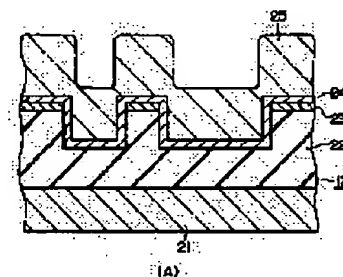
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## (54) ABRASIVE AND POLISHING METHOD

### (57)Abstract:

PURPOSE: To form a highly reliable conductor film at a high polishing speed by forming a film composed mainly of a metal on a substrate having recessed sections on the surface to fill up the recessed sections and suppressing the occurrence of dishing by using a chemimechanical polishing method using an abrasive containing a chemical reagent and etching agent.

CONSTITUTION: A substrate 12 to be polished is composed of a silicon substrate 21 and a silicon oxide film 22 and carbon film 23 successively formed on the substrate 21. After forming grooves for wiring, openings for continuous wiring, etc., in the film 22 by patterning the films 23 and 22, a titanium nitride film 24 and copper film are successively formed on the surface of the substrate 12. The copper film 25 have recessing and projecting sections which are formed in accordance with the steps provided on the surface of the silicon oxide film 22 which is the base film of the film 2. An abrasive is prepared by dispersing silica particles as abrasive particles in a mixed solution (Cu etching solution) of a glycine solution and hydrogen peroxide solution and adding benzotriazole (chemical reagent) to the mixed solution.



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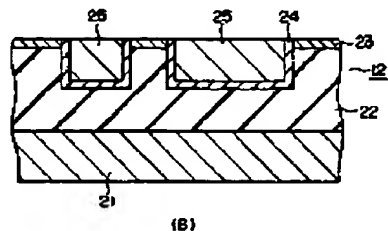
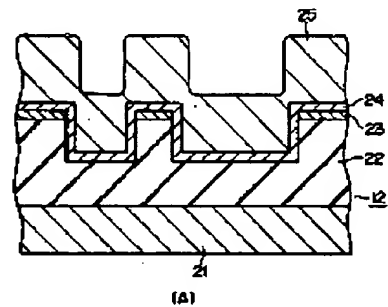
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(54) 【発明の名称】 研磨剤および研磨方法

(57) 【要約】

【目的】 本発明は、ディッシングの発生を抑制し、高い研磨速度で信頼性の高い導体膜を形成することができる研磨方法を提供することを目的とする。

【構成】 表面に凹部を有する基体上に前記凹部を充填するように金属を主成分とする材料からなる膜を形成する工程と、前記金属を主成分とする材料と反応することにより前記膜表面に保護膜を形成する化学試薬および前記金属を主成分とする材料のエッチング剤を含有する研磨剤を用いた化学機械的研磨方法により、前記膜を研磨して前記凹部内に導体膜を形成する工程とを具備することとを特徴としている。



化学試薬と、前記材料のエッチング剤とを含有することを特徴とする研磨剤。

【請求項 11】 アミノ酢酸および／またはアミド硫酸、酸化剤、水およびベンゾトリアゾールあるいはその誘導体を含有することを特徴とする研磨剤。

【発明の詳細な説明】

[ 0 0 0 1 ]

【産業上の利用分野】本発明は研磨剤および研磨方法に関する。特に半導体デバイス製造工程等の微細加工工程等において使用される研磨剤および研磨方法に関する。

[0002]

【従来の技術】近年、LSIの高集積化、高性能化のため、様々な微細加工技術が研究、開発されている。化学機械的研磨方法(ケミカルメカニカルポリッシング、以下CMPと省略する)は、そのような厳しい微細化の要求を満たすために研究されている技術の一つであり、これからの半導体デバイス製造工程、特に、多層配線形成工程における層間絶縁膜の平坦化、金属プラグ形成、埋め込み配線形成において必須の技術である。この方法は、例えば、C.W.Kaantaらや、K.D.Beyer らによって提案されている(CMTC Conference 1991 p.144 C.W.Kaanta et al., U.S. Patent No. 4944836 Beyer et al.)。

【0003】また、LSIの高速化の観点から、従来より上層配線に使用されているAlよりも低い抵抗を有するCuが新たな配線材料として検討されている。Cuは反応性イオンエッチングによる加工が困難であるので、Cuを配線材料として用いる場合にCMP技術を利用した埋め込み配線形成方法を採用することが検討されている。このような埋め込み配線形成方法は、例えば特開平2-278822号公報等により開示されている。この公報においては、研磨粒子、遷移金属のキレート塩、およびこの塩の溶剤からなる研磨スラリーを用いてCuを研磨することが開示されている。

[ 0 0 0 4 ]

【発明が解決しようとする課題】しかしながら、上記の埋め込み配線形成方法によりCuに傷を与えることなく高速で研磨しようとする場合には、研磨スラリー中におけるCuをエッチングする成分の量を多くしてCuのエッチングを強くする必要がある。このようにCuをエッチングする成分の量を多くすると、エッチングが等方的に進行して埋め込んだCuまで溶解してしまい、配線にディッシングが発生する。このため、信頼性の高いS<sub>1</sub>配線を形成するのが困難である。

【0005】また、CMP技術を利用したW配線形成においても、ディッシングが発生するので、信頼性の高いLSI配線を形成するのが困難である。さらに、CMP技術を利用したW（タングステン）配線形成においても研磨速度が遅い。

【０００６】本発明はかかる点に鑑みてなされたものであり、ディッシングの発生を抑制し、高い研磨速度で信

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【請求項 10】 金属を主成分とする材料と反応することにより、前記材料からなる膜表面に保護膜を形成する



座速度を得ることができる。

【0015】また、本発明は、上記研磨方法を達成するために、金属を主成分とする材料と反応することにより、前記材料からなる膜表面に保護膜を形成する化学試薬と、前記材料のエッチング剤とを含有することを特徴とする研磨剤を提供する。ここで、研磨剤としては、アミノ酢酸および／またはアミド硫酸、酸化剤、水およびベンゾトリアゾールあるいはその誘導体を含有する研磨剤が好ましい。

[0016]

【作用】本発明は、表面に凹部を有する基体上に前記凹部を充填するように金属を主成分とする材料からなる膜を形成し、前記金属を主成分とする材料と反応することにより前記膜表面に保護膜を形成する化学試薬および前記金属を主成分とする材料のエッチング剤を含有する研磨剤を用いた化学機械的研磨方法により、前記膜を研磨して前記凹部内に導体膜を形成することを特徴としている。

【0017】以下、金層を主成分とする材料がCu系材料であり、化学試薬がBTAである例を用いて本発明の作用を詳細に説明する。Cu膜にBTAを接触させた場合、Cu膜表面のCuまたはCu膜上に形成された自然酸化膜のCuOもしくはCu<sub>2</sub>OとBTAとが反応してCu(I)-BTAあるいはCu(II)-BTAで表されるCuキレート化合物からなる膜がCu膜または自然酸化膜上に強固に形成される。この膜は、Cuを腐食させるような雰囲気中もしくは溶液中、すなわちCuを高速でエッチングできる化学腐食域を有するエッチング剤の存在下において酸化または腐食を抑制する保護膜として作用する。また、この保護膜は、CMPの際に研磨粒子もしくは研磨パッドと物理的・機械的に接触することにより容易にしかも均一に除去される。このような保護膜がCuの酸化または腐食を抑制することは従来より知られていたが、CMPの際に研磨粒子もしくは研磨パッドと物理的・機械的に接触することにより容易にしかも均一に除去されることは本発明者らの研究により初めて明らかになった。

【0018】この保護膜は、図2（A）におけるCu膜25上全面に形成される。凸部に形成された保護膜は研磨粒子もしくは研磨パッドとの接触により容易に除去される。これにより露出したCu膜25の凸部はエッチング剤により高速にエッチングされる。このとき、Cu膜25の凹部に充填されているCu膜25は表面に保護膜が形成されているので、ほとんどエッチングされない。このようにして基体の凹凸形状に追従していたCu膜25の段差が小さくなる。その後、Cu膜25の凹部上に形成された保護膜は、研磨粒子もしくは研磨パッドと接触することにより除去される。この段階においては、Cu膜25には段差がほとんどない状態であるので、凹部に充填されているCu膜25が露出してエッチングが進

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んでもディッシングは起こらない。その結果、高速でCuを研磨して凹部のみに効率よくCuを残存させることができる。

【0019】なお、上記保護膜を除去する方法としては、研磨粒子もしくは研磨パッドと接触させる方法の他に、全周製あるいは樹脂製のブラシを接触させる方法、研磨剤を所定の圧力で吹き付ける方法が挙げられる。

【0020】一方、金属を主成分とする材料がW系材料であり、化学試薬がBPAである場合にも上記と同様に説明することができる。すなわち、W膜にBPAを接触させた場合、WやWO<sub>x</sub>とBPAとが反応してW-BPAで表されるWキレート化合物からなる膜がW膜上に強固に形成される。この膜は、Wを腐食させるような雰囲気中もしくは溶液中、すなわちWを高速でエッチングできる化学腐食域を有するエッチング剤の存在下において酸化または腐食を抑制する保護膜として作用する。また、この保護膜は、CMPの際に研磨粒子もしくは研磨パッドと物理的・機械的に接触することにより容易にしかも均一に除去される。

[0021]

【実施例】以下、本発明を図面を参照して具体的に説明する。

(実施例１) 図１は本発明の実施例において使用する研磨装置を示す概略図である。図中１１は回転可能な真空チャックホルダを示す。真空チャックホルダ１１には、被研磨基板１２がその被研磨面を研磨パッド１３と対向するようにして真空チャックされている。研磨パッド１３は、真空チャックホルダ１１の下方に配置された回転可能な研磨定盤１４上に取り付けられている。また、図示しない研磨剤タンクに接続された研磨剤供給配管１５の吐出部が研磨パッド１３近傍まで延出されている。この研磨剤供給配管１５は、研磨剤１６の供給量を制御する手段を備えている。なお、研磨パッド１３には、樹脂含浸不織布からなるものを用いた。

【００２２】図２（Ａ）は、本実施例で使用される被研磨基板１２を示す断面図である。この被研磨基板１２は次のようにして作製する。まず、シリコン基板２１上に厚さ１μm程度のシリコン酸化膜２２を形成し、その上に直流マグネトロンスパッタリング法により厚さ約１０nmの炭素膜２３を形成する。次いで、通常のフォトリソグラフィ工程および反応性イオンエッチング工程により、炭素膜２３およびシリコン酸化膜２２をパターンニングして、シリコン酸化膜２２に幅０．４～１．０μm、深さ０．４μmの配線用溝および接続配線用開孔等を形成する。次いで、直流マグネトロンスパッタリング法により厚さ５０nmの窒化チタン膜２４を形成し、引き続き直流マグネトロンスパッタリング法により厚さ約６００nmのＣｕ膜２５を形成する。図２（Ａ）に示すように、CMP直前のＣｕ膜２５は基体であるシリコン酸化膜２２に設けられた段差に追随しており凹凸形状を有す



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さ1  $\mu\text{m}$ 程度のシリコン酸化膜22を形成。次いで、通常のフォトリソグラフィ工程および反応性イオンエッチング工程により、シリコン酸化膜22をパターンニングして、シリコン酸化膜22に幅0.4~10  $\mu\text{m}$ 、深さ0.4  $\mu\text{m}$ の配線用溝および接続配線用開孔等を形成する。次いで、その上に、直流マグネトロンスパッタリング法により厚さ約20 nmのチタン膜31および厚さ約70 nmの窒化チタン膜24を形成し、引き続き六フッ化タンゲステン(WF<sub>6</sub>)ガスおよび水素ガスの混合ガスを用いた熱CVD法により、厚さ約600 nmのプラズマW膜32を形成する。図7(A)に示すように、CMP直前のW膜32は基体であるシリコン酸化膜22に設けられた段差に追従しており凹凸形状を有する。

【0035】このようにして作製した被研磨基板12を図1に示す研磨装置を用いてCMPを行い、配線用溝および接続配線用開孔以外の余剰なW膜32を除去してWの埋め込み配線およびWプラグを形成した。CMPに使用した研磨剤は、5体積%の過酸化水素水溶液に、研磨粒子としてアルミナ粒子(平均粒径50nm)を1.0重量%で分散させ、さらに0.4g/リットルのN-ベンゾイル-N-フェニルヒドロキシルアミン(化学試薬)を添加してなるものである。また、研磨条件は、研磨圧力300gf/cm<sup>2</sup>、研磨定盤14および真空チャックホルダ11の回転数100rpmとし、研磨定盤の温度を室温25℃で一定になるようにした。

【0036】CMPの結果、研磨速度は約300nm/分であり、非常に高速であった。また、W埋め込み配線およびWプラグを形成するために、W膜32と共にチタン膜31および窒化チタン膜24も除去しなければならない。チタン膜31および窒化チタン膜24の研磨速度はW膜25とほとんど同じ約300nm/分であったため、高速に除去することができた。また、CMP後のW埋め込み配線およびWプラグ、並びに露出したシリコン酸化膜の表面を走査型電子顕微鏡で観察したところ、図3に示すように、CMPにより発生したと思われる傷等は全く見られなかった。

【0037】なお、CMPにおいてW表面には、W、W<sub>2</sub>O<sub>3</sub>等が混在すると考えられるが、BPAはいずれの物質ともキレート化合物を形成して保護膜を設ける。次に、ディッシング量の配線幅依存性について調べた。その結果を図8に示す。ここでは、凸部のW膜32、チタン膜31および窒化チタン膜24をすべて除去した時を研磨終了時とした。図8から明らかなように、W埋め込み配線のディッシング値は、配線幅が10μmの配線中央部で約50nmであり、実用上はほぼ問題のない程度であった。また、研磨時間をさらに延長しても、ディッシ

ング値はほとんど増加しなかったことを考慮すると、W膜32上に形成された保護膜が効果的に機能していることが分かる。

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【0038】本実施例においては、被研磨膜としてW膜を用いた場合について説明しているが、Wに少量の不純物や添加元素が含有されている場合においても同様の効果が得られる。

【0039】さらに、上記実施例では、被研磨体として、W膜をブランケット状に形成する場合において説明しているが、WF<sub>6</sub>ガスとSiH<sub>4</sub>ガスとの混合ガス、もしくはこの混合ガスにH<sub>2</sub>ガスを添加したガスを用いてW膜の選択成長を行う場合に対しても本発明は適用可能である。すなわち、例えばコンタクトホールやビアホールを有する層間絶縁膜の底に露呈するシリコン層やTiN層、TiSi<sub>2</sub>等のシリサイド層等の上に選択的にW膜を成長させる場合において、選択性の崩れにより、絶縁膜表面にW粒子が成長することがあるが、上記実施例の研磨方法を用いれば、このW粒子を選択的に除去することが可能である。

【0040】また、本実施例においては、研磨粒子としてアルミナ粒子のみを用いた場合について説明しているが、研磨粒子としてアルミナ粒子と同等あるいはそれ以上の硬度を有するシリカ粒子、酸化チタン粒子、酸化ジルコニウム粒子、酸化セリウム粒子、炭化硅素粒子、ダイヤモンド粒子等を用いた場合においても同様の効果が得られる。

【0041】また、本実施例においては、エッチング剤として過酸化水素水溶液を用い、化学試薬としてBPAを用いた場合について説明しているが、エッチング剤として硝酸鉄水溶液、フェリシアン化カリウムとエチレンジアミンとの混合水溶液、フェリシアン化カリウムとリン酸との混合水溶液等を用いた場合においても同様の効果が得られる。また、化学試薬としては、エッチングする膜材料に応じてこの材料とキレート化合物や錯体化合物を形成する試薬、例えばBPAの各種誘導体等を用いた場合においても同様の効果が得られる。

【0042】また、本実施例においては、研磨パッドには樹脂含浸不織布からなる研磨パッドを用いたが、同程度の硬度を有するものであれば良く、例えば、ポリエステル、ポリエーテル等の不織布、発泡ポリウレタンパッド、またはそれら2種類以上の異なるパッドを張り合わせた研磨パッド等を用いてもよい。なお、上記した各種物質の誘導体としては、水素部分がアルキル基（メチル基、エチル基等）に置き変わったものが特に好ましい。

（比較例2）研磨剤として、5体積%の過酸化水素水溶液に、研磨粒子としてアルミナ粒子（平均粒径50nm）を1.0重量%で分散させたもの、すなわち実施例で使用した研磨剤においてBPAを添加していないものを用いること以外は実施例2と同様にして図7（A）に示す被研磨基板12にCMPを行った。

【0043】CMPの結果、研磨速度は約350nm/分であり高速であるが、ディッシング値が実施例2の場合に比べて非常に大きかった。すなわち、図9に示すよ

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うに、最小線幅の0.4μm配線幅においてはディッシング量が約200nmであり、さらに、熱CVD時に形成される配線中央部のW膜の合わせ目に沿ってエッチングが進行し、配線に穴33が開いた状態になった。

（実施例3）本発明の研磨方法においては、研磨中に金属層、例えばCuの表面に、化学試薬、例えばBTAと金属との化合物（Cu-BTA）からなる保護膜が形成される。この場合、保護膜が機械的に除去された時点で研磨剤中のエッチング成分によりCuがエッチングされる。この場合、Cuのエッチング速度の活性化エネルギーE<sub>a</sub>は比較的大きく、Cuの研磨速度の活性化エネルギーE<sub>a</sub>は比較的小さい。これは、研磨においては、化学的作用だけでなく機械的作用も含まれるからである。したがって、E<sub>a</sub>>E<sub>a</sub>の関係が成り立つ。このため、研磨速度/エッチング速度の比の値は低温ほど大きくなるので、ディッシング低減の観点からは低温でCMPを行った方が有利になる。

【0044】そこで、本実施例では、CMPを低温で行う場合について説明する。CMPを低温、例えば20℃以下で行う場合には、研磨定盤、研磨パッド、および研磨剤のうち少なくとも一つを冷却してもよく、始めに通常の温度（常温）で第一段階の研磨を行い、続けて低温、例えば20℃以下で第二段階の研磨を行ってもよい。

【0045】図2（A）に示す被研磨基板12を図1に示す研磨装置を用いてCMPを行い、配線用溝および接続配線用開孔以外の余剰なCu膜25を除去してCuの埋め込み配線およびCuプラグを形成した。CMPに使用した研磨剤は、0.12モル/リットルのグリシン（C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N）水溶液と0.44モル/リットルの過酸化水素水（H<sub>2</sub>O<sub>2</sub>）との混合溶液（Cuのエッチング剤）に、研磨粒子としてシリカ粒子（平均粒径30nm）を5.3重量%で分散させ、さらに0.001モル/リットルのベンゾトリアゾール（C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>）（化学試薬）を添加してなるものである。また、研磨条件は、研磨圧力400gf/cm<sup>2</sup>、研磨定盤14および真空チャックホルダ11の回転数60rpmとした。

【0046】このときのCuの研磨速度およびエッチング速度の温度依存性を調べた。その結果を図10に示す。なお、温度は約-2℃から約100℃まで変化させた。図10から明らかなように、研磨速度およびエッチング速度は、温度の逆数（1/T）のexponential（指数）に比例した。これらのグラフの傾きから研磨速度の活性化エネルギーE<sub>a</sub>およびエッチング速度の活性化エネルギーE<sub>a</sub>をそれぞれ求めると、E<sub>a</sub>が約0.7eVであり、E<sub>a</sub>が約0.9eVであった。それぞれのグラフの傾きは負であり、E<sub>a</sub><E<sub>a</sub>であることから、研磨速度/エッチング速度の比の値は低温ほど大きくなる。したがって、CMPの温度が低温であるほど、Cu配線のディッシング量が減少する。



【0047】次に、研磨温度を室温（24.0℃）に設定してCMPを行った場合と、研磨温度を14.0℃に設定してCMPを行った場合のそれぞれのディッシング量の配線幅依存性について調べた。その結果を図11に示す。ここでは、凸部上のCu膜25および窒化チタン膜24をすべて除去した時を研磨終了時とした。図10から明らかなように、Cu埋め込み配線のディッシング値は、配線幅が10μmの配線中央部で約100nmであり、実用上は問題のない程度であった。

【0048】次に、研磨温度を室温（24.0℃）に設定してCMPを行った場合と、研磨温度を14.0℃に設定してCMPを行った場合の被研磨5μmのディッシング量の研磨時間依存性について調べた。その結果を図12に示す。図12から明かなように、低温でCMPを行うことにより、オーバーポリッシング時のディッシング量の増加を抑制することができる。

【0049】また、CMP後のCu埋め込み配線およびCuプラグの表面を走査型電子顕微鏡で観察したところ、図2（B）に示すように、CMPにより発生したと思われる傷等は全く見られなかった。

【0050】本実施例においては、被研磨膜としてCu膜を用いた場合について説明しているが、Cuに少量の不純物や添加元素が含有されている場合や、被研磨膜としてCu以外の金属、例えばAg、Al、W等の膜やこれらを主成分とした膜を用いた場合においても同様の効果が得られる。

【0051】また、本実施例においては、研磨粒子としてシリカ粒子のみを用いた場合について説明しているが、研磨粒子としてシリカ粒子と同等あるいはそれ以上の硬度を有するアルミナ粒子、酸化チタン粒子、酸化ジルコニウム粒子、酸化セリウム粒子、炭化珪素粒子、ダイヤモンド粒子等を用いた場合においても同様の効果が得られる。

【0052】また、本実施例においては、エッチング剤としてグリシン水溶液および過酸化水素水の混合溶液を用い、化学試薬としてBTAを用いた場合について説明しているが、エッチング剤としてアミド硫酸もしくはアミノ酢酸とアミド硫酸の混合酸と、過酸化水素(H<sub>2</sub>O<sub>2</sub>)、硝酸、次亜塩素酸、オゾン水等の酸化剤とからなるもの、アンモニア、硝酸アンモニウム、塩化アンモニウム、クロム酸等を用いた場合においても同様の効果が得られる。また、化学試薬としては、エッチングする膜材料に応じてこの材料とキレート化合物や錯体化合物を形成する試薬、例えばBTAの各種誘導体、これらを含む混合物、チオ尿素、チオ尿素誘導体、クペロン、ベンゾイミダゾール、トリアゾール、サリチルアルドキシム、エチレンジアミン、システイン、p-アミノベンズアルデヒド、ハロ酢酸、ドデシルメルカプタン、ホスホン酸類、グルコースやフルクトース等の単糖類等を用いた場合においても同様の効果が得られる。特に、BTA

またはBTAの各種誘導体は、硫酸水溶液や塩酸水溶液等を用いる場合に有効である。

【0053】また、本実施例においては、研磨パッドには樹脂含浸不織布からなる研磨パッドを用いたが、同程度の硬度を有するものであれば良く、例えば、ポリエステル、ポリエーテル等の不織布、発泡ポリウレタンパッド、またはそれら2種類以上の異なるパッドを張り合わせた研磨パッド等を用いてもよい。なお、上記した各種物質の誘導体としては、水素部分がアルキル基等に置き変わったものが特に好ましい。

(実施例４) 図１３は本発明の研磨方法に使用する研磨装置の一部を示す概略図である。この研磨装置においては、研磨定盤１４内に冷媒循環路４１が設けられている。この冷媒循環路４１内に水、エチレングリコール等の冷媒を流通させることにより、研磨定盤１４および研磨パッド１３の温度を調節することができる。研磨定盤の主要部分の材質はグラスファイバーであり、金属材料と比較して熱容量が小さく、熱伝導率が高いので、迅速な温度調節が可能である。冷媒循環路４１は２系統の冷媒冷却装置（冷却器４２、４３）に接続されており、途中の切り替えスイッチ４４で随時、冷媒の循環経路を切り替えることができるようになっている。さらに、冷却器４２および４３には、それぞれ研磨剤供給系統４５および４６がそれぞれ接続されており、供給する研磨剤の温度を調節できるようになっている。また、研磨定盤１４の上方には、冷却された純水を研磨定盤１４上に吹き付けるジェットノズル４７が配置されている。

【0054】上記構成を有する研磨装置を用いて、二段階の研磨、すなわち第一の研磨（室温研磨）および第二の研磨（低温研磨）でCMPを行った。なお、冷却器42の設定温度を24.0℃とし、冷却器43の設定温度を14.0℃とすることにより、研磨剤供給系統45およびその内部の研磨剤の温度を24.0℃に温度調節し、研磨剤供給系統46およびその内部の研磨剤の温度を14.0℃に温度調節した。また、ジェットノズル47内部の純水の温度も14.0℃に温度調節した。

【0055】まず、切り替えスイッチ44により研磨定盤14の冷媒循環路41を冷却器42に接続し、研磨剤供給系統45を用いて、研磨温度を24.0℃に設定し、実施例3と同様にしてCMPを行った。このとき、研磨時間は、研磨終了時間の約80%とした。その結果、研磨終了時間が2分37秒であったので、単一の研磨の研磨時間は2分5秒であった。

【0056】第一の研磨の後、研磨削供給系統45を停止し、研磨定盤14の冷循環回路41を切り替えスイッチ44により冷却器43に接続し、急速に研磨定盤14内に14、0℃の冷却水を循環させると共に、ジェットノズル47から冷却された純水を噴射することにより、研磨定盤14を冷却した。研磨定盤14上の研磨パッド13表面の温度が約14℃になった時点で、研磨削供給

[0058]

【図面の簡単な説明】

【図4】本発明の研磨方法におけるBTAの添加量に対する研磨速度およびエッチング速度の変化を示すグラフ

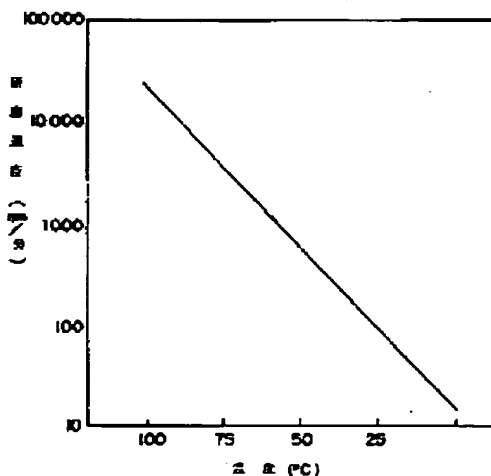
10 【図9】従来の研磨方法を説明するための断面図。

【図 14】本発明の研磨方法における配線幅とディッシング量との関係を示すグラフ。

【符号の説明】

11…真空チャックホルダ、12…被研磨基板、13…研磨パッド、14…研磨定盤、15…研磨剤供給配管、16…研磨剤、21…シリコン基板、22…シリコン酸化膜、23…炭素膜、24…窒化チタン膜、25…Cu膜、31…チタン膜、32…W膜、41…冷媒循環路、42、43…冷却器、44…切り替えスイッチ、45、46…研磨剤供給系統、47…ジェットノズル。

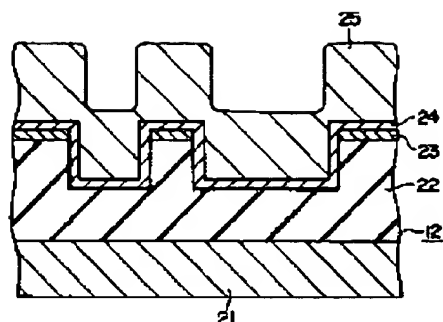
【圖3】



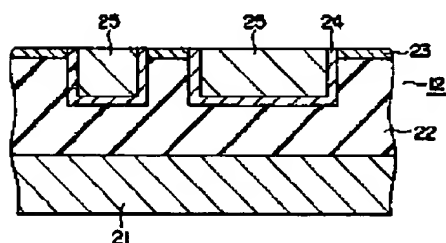
(10)

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【圖2】

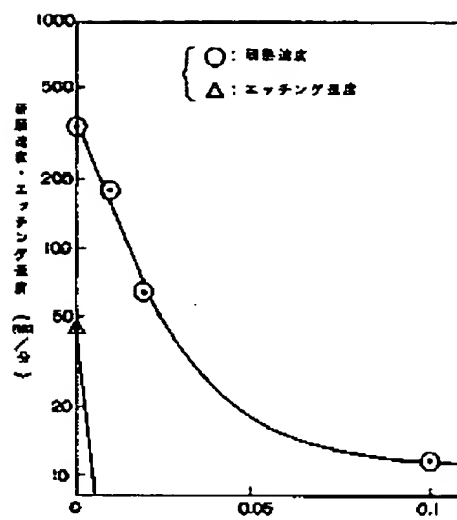


(A)



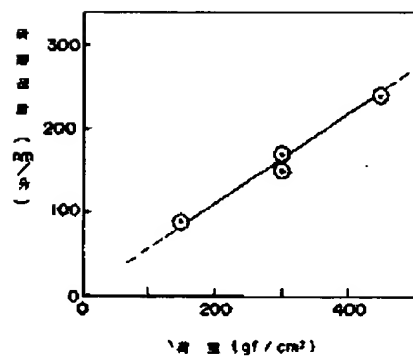
(B)

【図4】

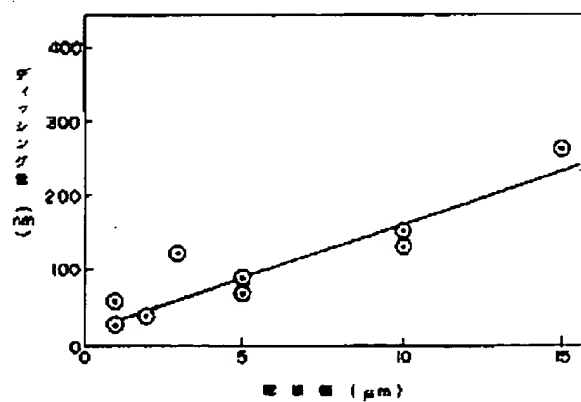


グリシン/ $H_2O_2$  溶液にグアニル 0.12 モル/リットル) に加える BTA の濃度のグリシン濃度に対する比率

【图5】



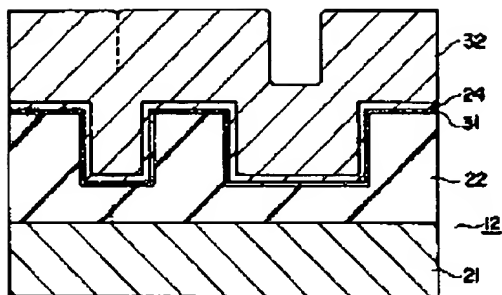
【圖6】



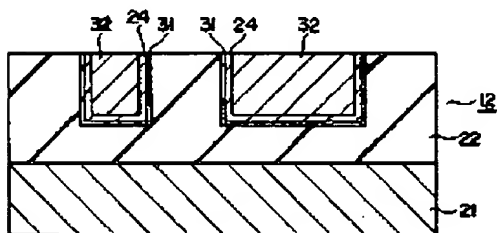
(11)

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【図7】

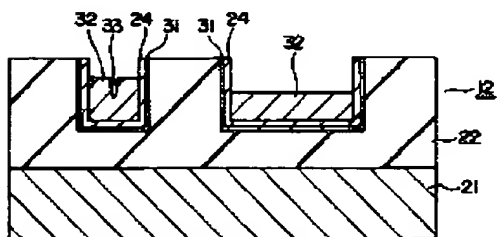


(A)

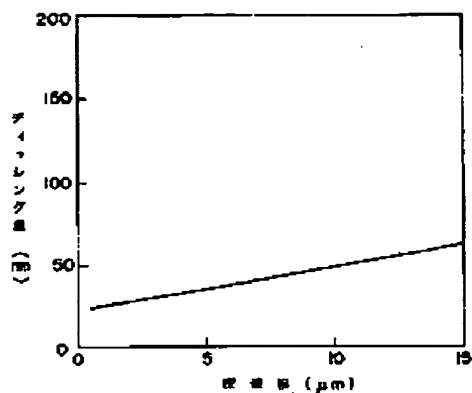


(B)

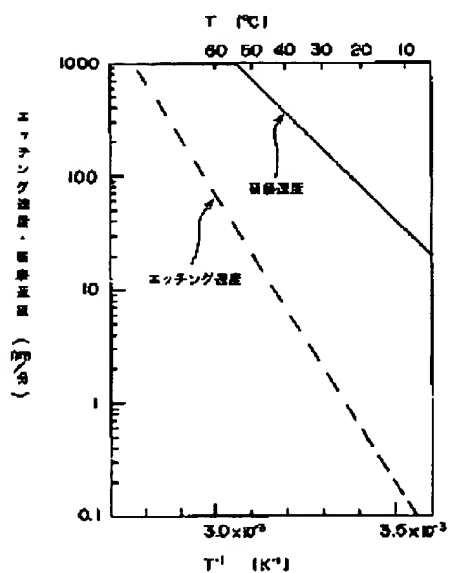
【図9】



【図8】



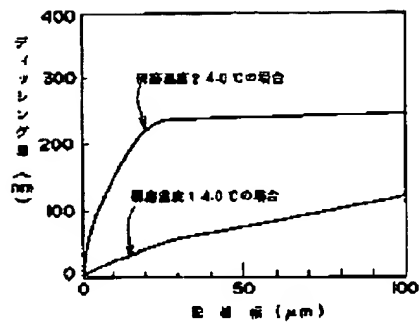
【図10】



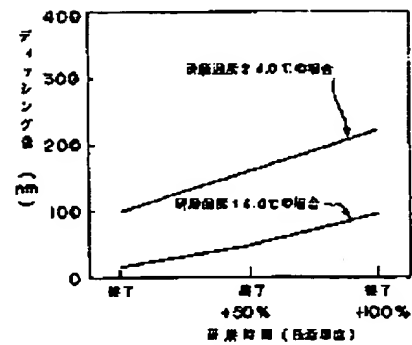
(12)

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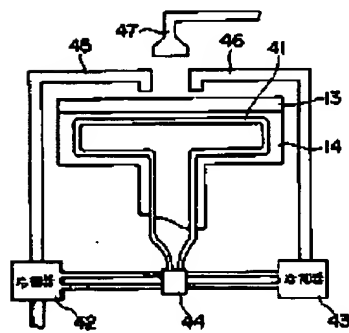
【图 11】



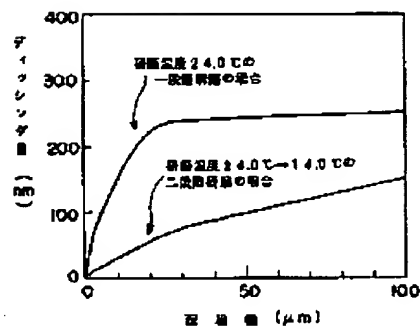
【图 12】



【圖 13】



【图 14】



フロントページの続き

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 【国際特許分類第7版】  
 H01L 21/304 321

【手続補正言】  
【提出日】平成12年10月13日（2000. 10. 13）  
【手続補正1】  
【補正対象音類名】明細書  
【補正対象項目名】特許請求の範囲  
【補正方法】変更  
【補正内容】  
【特許請求の範囲】

【請求項5】前記エッチング剤中のアミノ酢酸および／

【請求項 11】 アミノ酢酸および／またはアミド酸、

前記金属を主成分とする材料とアミノ酢酸、アミド硫酸、または過酸化水素との反応により前記導電性膜の表

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the abrasive material and the polishing technique which are used in micro-processing processes, such as a semiconductor-device manufacturing process, etc. about an abrasive material and the polishing technique.

[0002]

[Description of the Prior Art] In recent years, various micro-processing techniques are studied and developed for high integration of LSI, and highly-efficient-izing. The chemical machinery-polishing technique (it abbreviates to a chemical mechanical polishing and following CMP) is one of the techniques currently studied in order to fill a demand of such severe detailed-izing, and is indispensable technique in a future semiconductor-device manufacturing process, the flattening of the layer insulation layer especially in a multilayer-interconnection formation process, metal plug formation, and embedding wiring formation. this technique -- for example, C.W.Kaanta et al. and KD.Beyer \*\* -- it is proposed (VMIC Conference 1991 p.144 C.W.Kaanta et.al., U.S.PatentNo.4944836 Beyer et.al.)

[0003] Moreover, it inquires from the viewpoint of improvement in the speed of LSI as a wiring material with Cu newer than the former which has resistance lower than aluminum currently used for the upper wiring. Since the manipulation by reactive ion etching is difficult for Cu, when using Cu as a wiring material, the thing using CMP, technique for which it embeds and the wiring formation technique is adopted is examined. Such embedding wiring formation technique is indicated by JP,2-278822,A etc. In this official report, grinding Cu using the polishing slurry which consists of polishing grain, a chelate salt of transition metals, and a solvent of this salt is indicated.

[0004]

[Problem(s) to be Solved by the Invention] However, when it is going to grind at high speed, without giving a blemish to Cu by the above-mentioned embedding wiring formation technique, it is necessary to make [ many ] the amount of the component which etches Cu in a polishing slurry, and to strengthen etching of Cu. Thus, if the amount of the component which etches Cu is made many ], it will melt to Cu which etching advanced isotropic and embedded, and a dishing will occur in a wiring. For this reason, it is difficult to form reliable LSI wiring.

[0005] Moreover, also in W wiring formation using CMP technique, since a dishing occurs, it is difficult to form reliable LSI wiring. Furthermore, also in W (tungsten) wiring formation using CMP technique, a polishing speed is slow.

[0006] this invention is made in view of such a point -- having -- occurrence of a dishing -- suppressing -- a high polishing speed -- a reliable conductor -- it aims at offering the abrasive material and the polishing technique of forming a layer

[0007]

[Means for Solving the Problem] When forming an embedding metal wiring, beer, or a contact by generally performing polishing processing to the base which has the shape of a toothing, only the heights of a ground layer is ground and it is important only for the concavity to make the target layer remain. If only mechanical polishing performs this polishing processing, things can be carried out, namely, although a high selection ratio is obtained, mechanical polishing has a slow polishing speed and cannot secure the throughput whose target layer is made to remain efficiently and which is needed by the semiconductor-device manufacturing process only to a concavity. On the other hand, in order that etching may progress isotropic although a polishing speed is quick if only chemical polishing performs this polishing processing, the target layer cannot be made to remain only in a concavity. Then, this invention persons examined in detail CMP which combined mechanical polishing and chemical polishing, and clarified the component contributed to mechanical polishing among abrasive materials, and the component contributed to chemical polishing. This invention persons and by performing CMP into the material of the layer made into the purpose using the abrasive material containing a specific chemical agent based on this consideration the target layer top -- a protection layer -- forming -- isotropic chemical polishing -- suppressing -- this protection layer -- the heights front face of a ground layer -- setting -- mechanical polishing -- easy -- removing -- a reliable conductor -- it finds out that a layer can be formed and came to carry out this invention

[0008] Namely, the process which forms the layer which consists of a material which makes a metal a principal component so that this invention may be filled up with the aforementioned concavity on the base which has a concavity on a front face, By the chemical machinery-polishing technique using the abrasive material containing the etching agent of the material which makes a principal component the chemical agent and the aforementioned metal which form a protective coat in the aforementioned layer



front face by reacting with the material which makes the aforementioned metal a principal component the aforementioned layer -- grinding -- the inside of the aforementioned concavity -- a conductor -- the polishing technique characterized by providing the process which forms a layer is offered

[0009] Here, the substrate which consists of compound semiconductors, such as a silicon substrate, a glass substrate for TFT-LCD, and GaAs, as a base can be used. The concavity on the front face of a base is used as the wiring section, the beer, or the contact hole of an embedding metal wiring.

[0010] As a material which makes a metal a principal component, that in which Cu, Cu alloy, Ag, Ag alloy, aluminum, aluminum alloy, W, W alloys, these oxides, the impurity little to these metals, and the alloying element are contained can be used. moreover, as a chemical agent which forms a protective coat by reacting with this material What [ replaced the benzotriazol (it abbreviates to BTA hereafter), and BTA derivative, for example, one hydrogen atom of the benzene ring of BTA, by the methyl group ] (tolyl triazole (TTA)) Also especially in the mixture containing these, thiourea, and an azole The benzimidazole, A triazole, a salicylaldoxime, a cupferron, ethylenediamine, The amino acid containing sulfur especially a cystine, a p-amino benzaldehyde, \*\*\*\*\*,s, such as a halo acetic acid, thiols, for example, a dodecyl mercaptan, and an octane \*\*\*\*\* acid, -- acids -- Monosaccharides, such as a glucose and a fructose, and the derivatives of these matter or those mixture, an N-benzoyl-N-phenyl hydroxylamine (it abbreviates to BPA hereafter), BPA derivative, etc. can be used. Moreover, to a chemical agent, the organic compound which has a canal fraction (hydrophobic) is desirable. What replaced BTA and BTA derivative, for example, one hydrogen atom of the benzene ring of BPA, by the methyl group, and the mixture containing these demonstrate an effect, especially when the material which makes a metal a principal component is Cu or Cu alloy. Moreover, BPA, BPA derivatives, and such mixture demonstrate an effect, especially when the material which makes a metal a principal component is W or W alloy.

[0011] The etching agent of the material which makes a metal a principal component can be suitably chosen by the material. For example, the etching agent containing oxidizers, such as aminoacetic acids, such as a glycine, amidosulfuric acids or these mixed acids, a hydrogen peroxide ( $H_2O_2$ ) and a nitric acid, a hypochlorous acid, and ozone water, is used. Moreover, the aqueous solutions, such as chromic acids, such as a nitric acid, ammonia, ammonium salts, for example, an ammonium persulfate, an ammonium nitrate, and an ammonium chloride, can also be used. These etching agents have especially the desirable thing used when the material which makes a metal a principal component is Cu or Cu alloy.

[0012] Moreover, when the material which makes a metal a principal component is W or W alloy, as an etching agent, a hydrogen-peroxide-solution solution, the iron nitrate aqueous solution, the mixed aqueous solution of a red potassium prussiate and ethylenediamine, the mixed aqueous solution of a red potassium prussiate and a phosphoric acid, etc. can be used.

[0013] As for the protective coat in which the material and chemical agent which make a metal a principal component react to, and are formed, it is desirable to include a metaled chelate compound or a metaled complex compound. In this invention, CMP may be performed using the abrasive material containing the above-mentioned chemical agent and an etching agent, and may be performed using the abrasive material which contains the above-mentioned etching agent and does not contain the above-mentioned chemical agent as the 1st phase, and may be performed using the aforementioned abrasive material which added the above-mentioned chemical agent as the 2nd phase after that. The technique of preparing two or more nozzles for abrasive-material supply as the technique of adding a chemical agent to an abrasive material in CMP in the case of the latter, supplying the aqueous solution which contains a chemical agent from the feed hopper prepared in the nozzle or the turn table with another technique of distinguishing and using nozzle for abrasive materials used in the 1st phase and nozzle for abrasive materials used in the 2nd phase and nozzle for abrasive materials, and mixing with an abrasive material on a turn table is mentioned.

[0014] Moreover, in this invention, since there are many components contributed to chemical polishing among abrasive materials, a still high polishing speed can be obtained by heating the fraction which an abrasive material and a ground layer contact.

[0015] Moreover, this invention offers the abrasive material characterized by containing the chemical agent which forms a protective coat in the layer front face which consists of the aforementioned material, and the etching agent of the aforementioned material by reacting with the material which makes a metal a principal component, in order to attain the above-mentioned polishing technique. Here, as an abrasive material, the abrasive material containing an aminoacetic acid and/or an amidosulfuric acid, an oxidizer, water and a benzotriazol, or its derivative is desirable.

[0016]

[Function] this invention forms the layer which consists of a material which makes a metal a principal component so that it may be filled up with the aforementioned concavity on the base which has a concavity on a front face. By the chemical machinery-polishing technique using the abrasive material containing the etching agent of the material which makes a principal component the chemical agent and the aforementioned metal which form a protective coat in the aforementioned layer front face by reacting with the material which makes the aforementioned metal a principal component the aforementioned layer -- grinding -- the inside of the aforementioned concavity -- a conductor -- it is characterized by forming a layer

[0017] Hereafter, the material which makes a metal a principal component is Cu system material, and a chemical agent explains an operation of this invention in detail using the example which is BTA. When BTA is contacted on Cu layer, the layer which consists of a Cu chelate compound which BTA reacts as  $CuO$  or  $Cu_2O$  of a natural-oxidation layer formed on Cu of Cu layer front face or Cu layer, and is expressed with  $Cu(I)$ -BTA or  $Cu(II)$ -BTA is firmly formed on Cu layer or a natural-oxidation layer. This layer acts as a protective coat which suppresses oxidization or the cauterization in the ambient atmosphere which makes Cu corrode, or a solution (i.e., the bottom of presence of the etching agent which has the chemical-etching region which can etch Cu

at high speed). Moreover, this protective coat is removed easily and uniformly by contacting polishing grain or a polishing pad physically and mechanically in the case of CMP. Although it was known conventionally that such a protective coat will suppress oxidization or the cauterization of Cu, being removed easily and uniformly became clear for the first time by research of this invention persons by contacting polishing grain or a polishing pad physically and mechanically in the case of CMP.

[0018] This protective coat is formed all over the Cu layer 25 top in drawing 2 (A). The protective coat formed in the heights is easily removed by the contact to polishing grain or a polishing pad. In the heights of the Cu layer 25 which this exposed, it is etched at high speed by the etching agent. Since, as for the Cu layer 25 with which the concavity of the Cu layer 25 is filled up, the protective coat is formed in the front face at this time, it is hardly etched. Thus, the level difference of the Cu layer 25 followed in the shape of [ of a base ] a toothing becomes small. Then, the protective coat formed on the concavity of the Cu layer 25 is removed by contacting polishing grain or a polishing pad. In this phase, since it is in the status which does not almost have a level difference in the Cu layer 25, although the Cu layer 25 with which the concavity is filled up is exposed and etching progresses, a dishing does not happen. Consequently, Cu can be ground at high speed and Cu can be made to remain efficiently only in a concavity.

[0019] In addition, the technique of contacting the brush made from metal or a resin other than the technique of making polishing grain or a polishing pad contacting, as technique of removing the above-mentioned protective coat, and the method of spraying an abrasive material by the predetermined pressure are mentioned.

[0020] On the other hand, the material which makes a metal a principal component is W system material, and when a chemical agent is BPA, it can be similarly explained as the above. That is, when BPA is contacted on W layer, the layer which consists of a W chelate compound which W, and  $WO_x$  and BPA react and is expressed with W-BPA is firmly formed on W layer. This layer acts as a protective coat which suppresses oxidization or the cauterization in the ambient atmosphere which makes W corrode, or a solution (i.e., the bottom of presence of the etching agent which has the chemical-etching region which can etch W at high speed). Moreover, this protective coat is removed easily and uniformly by contacting polishing grain or a polishing pad physically and mechanically in the case of CMP.

[0021]

[Example] Hereafter, this invention is concretely explained with reference to a drawing.

(Example 1) View 1 is the schematic diagram showing the polishing equipment used in the example of this invention. 11 in drawing shows the vacuum-chuck electrode holder which can be rotated. In the polished surface-ed, as the ground substrate 12 counters the vacuum-chuck electrode holder 11 with the polishing pad 13, the vacuum chuck is carried out to it. The polishing pad 13 is attached on the turn table 14 which has been arranged underneath the vacuum-chuck electrode holder 11 and which can be rotated. Moreover, the regurgitation section of the abrasive-material charging line 15 connected to the abrasive-material tank not to illustrate has extended even to about 13 polishing pad. This abrasive-material charging line 15 is equipped with a means to control the amount of supply of an abrasive material 16. In addition, what consists of a resin sinking-in nonwoven fabric was used for the polishing pad 13.

[0022] Drawing 2 (A) is a cross section showing the ground substrate 12 used by this example. This ground substrate 12 is produced as follows. First, the silicon oxide 22 with a thickness of about 1 micrometer is formed on a silicon substrate 21, and the carbon film 23 with a thickness of about 10nm is formed by the direct-current magnetron sputtering method on it. Subsequently, according to a usual photo-lithography process and a usual reactive-ion-etching process, patterning of the carbon film 23 and the silicon oxide 22 is carried out, and the slot for a wiring with a width of face [ of 0.4-10 micrometers ] and a depth of 0.4 micrometers, puncturing for a connection wiring, etc. are formed in a silicon oxide 22. Subsequently, the titanium-nitride layer 24 with a thickness of 50nm is formed by the direct-current magnetron sputtering method, and the Cu layer 25 with a thickness of about 600nm is succeedingly formed by the direct-current magnetron sputtering method. As shown in drawing 2 (A), the Cu layer 25 in front of CMP follows the level difference prepared in the silicon oxide 22 which is a base, and has the shape of a toothing.

[0023] Thus, CMP was performed using the polishing equipment to which the produced ground substrate 12 is shown in drawing 1, the slot for a wiring and the Cu layer [ surpluses / other than puncturing for a connection wiring ] 25 were removed, and an embedding wiring and Cu plug of Cu were formed. The abrasive material used for CMP to the mixed solution (etching agent of Cu) of the 0.12 mols [ / l. ] glycine ( $C_2H_5O_2N$ ) aqueous solution and 0.44 mols [ / l. ] hydrogen peroxide solution ( $H_2O_2$ ) Silica grain (30nm of mean particle diameters) is distributed at 5.3 % of the weight as polishing grain, and it comes to add a 0.001 more mols [ / l. ] benzotriazol ( $C_6H_5N_3$ ) (chemical agent). Moreover, polishing conditions are set to rotational frequency 100rpm of polishing pressure force 300gf/cm<sup>2</sup>, the turn table 14, and the vacuum-chuck electrode holder 11, and were made to become fixed about the temperature of a turn table at the room temperature of 25 degrees C.

[0024] As a result of CMP, the polishing speed was a part for about 120nm/, and was very high-speed. Moreover, in order to form Cu embedding wiring and Cu plug, you also have to remove the titanium-nitride layer 24 prepared on the heights of the Cu layer 25 with the Cu layer 25. Although the polishing speed of the titanium-nitride layer 24 is a part for about 30nm/later than the polishing speed of the Cu layer 25, as mentioned above as an operation of this invention, when polishing of the Cu layer 25 progresses more slightly than polishing of the titanium-nitride layer 24, since the fraction of the Cu layer 25 serves as a concavity as compared with titanium-nitride layer 24 fraction, on the front face of the Cu layer 25, a protective coat is formed and polishing of Cu layer does not progress any more. For this reason, the titanium-nitride layer 24 was also removable good. Moreover, when the front face of Cu embedding wiring after CMP and Cu plug was observed by the scanning electron microscope, as shown in drawing 2 (B), the blemish considered to have generated by CMP was not seen at all.

[0025] In addition, since Cu front face contacts water in CMP, although to intermingle Cu, CuO, Cu<sub>2</sub>O, Cu(OH)<sub>x</sub>, etc. is

considered by the front face of the Cu layer 25, which matter forms a chelate compound and BTA prepares a protective coat. [0026] Next, the temperature dependence of the polishing speed to Cu was investigated using the abrasive material which added BTA. At this time, the polishing pressure force is 400gf/cm<sup>2</sup>. It carried out and both the rotational frequencies of a turn table and a vacuum-chuck electrode holder were set to 60rpm. The result which set the quadrature axis as an axis of ordinate and the inverse number (1/T) of temperature, and plotted the logarithm of a polishing speed is shown in drawing 3. It sets by about 100 degrees C from the temperature of about 0 degree C, and it is plotted on about 1 straight line, and the inclination serves as the inverse number (1/T) of the temperature which a polishing speed receives with negative so that clearly from drawing 3. It is proportional to an exponent. Therefore, rate-limiting [ of the polishing speed ] is carried out by a certain chemical reaction which mainly happens into CMP, and to hardly be influenced is considered by the physical and mechanical element. This means that the protective coat formed in Cu layer 25 front face is easily removed in CMP by physical / mechanical operation by polishing grain or the polishing pad.

[0027] Moreover, it investigated about change of the polishing speed and etch rate to the addition of BTA. The result is shown in drawing 4. In the graph of drawing 4, a quadrature axis expresses the addition of BTA to glycine 0.12mol/l., and an axis of ordinate expresses a polishing speed and an etch rate. In not adding BTA so that clearly from drawing 4, although about 350nm a part for /and an etch rate are high, if the polishing speed adds BTA with a part for about 45nm/, both a polishing speed and an etch rate will decrease exponentially. However, it is thought that the polishing speed is mostly saturated with BTA 0.1mol/l. Moreover, it turns out that the amount of BTA required in order to protect the Cu layer 25 is good in very few amount of 0.001 mols/l. or less.

[0028] Next, BTA was investigated about the pressure (load) dependency of a polishing speed using the abrasive material added 1. 0.001 mols /. At this time, the temperature of a turn table was made to become fixed at 25 degrees C, and both the rotational frequencies of a turn table and a vacuum-chuck electrode holder were set to 60rpm. The result is shown in drawing 5. A polishing speed is in a proportionality to the polishing pressure force, and it is thought that the straight line passes along the zero of the graph of drawing 5 so that clearly from drawing 5. That is, in the domain of the polishing pressure force applied in usual CMP, it is thought that rate-limiting [ of the polishing speed ] is carried out to the speed by which rate-limiting is carried out to the polishing pressure force and from which in other words the protective coat of Cu layer 25 front face is removed in physical / mechanical operation with polishing grain or a polishing pad. Therefore, it is possible to raise to the value of the polishing speed in each temperature which shows a polishing speed in drawing 3 by making the polishing pressure force high.

[0029] Next, it investigated about the wiring width-of-face dependency of the amount of dishings. The result is shown in drawing 6. Here, the time of removing altogether the Cu layer 25 and the titanium-nitride layer 24 of a heights was considered as the time of a polishing end. Wiring width of face was about 150nm in the wiring center section which is 10 micrometers, and the dishing value of Cu embedding wiring was a grade which is mostly satisfactory practically so that clearly from drawing 6. Moreover, even if it extends polishing time further, a dishing value understands that the protective coat formed on the Cu layer 25 is functioning effectively, when it takes having hardly increased into consideration.

[0030] In this example, although the case where Cu layer is used as a ground layer is explained, when a little impurity and a little alloying element contain in Cu, or when layers, such as metals other than Cu, for example, Ag, aluminum, W, etc., and the layer which made these the principal component are used as a ground layer, the same effect is acquired.

[0031] Moreover, in this example, although the case where only silica grain was used as polishing grain was explained, when the alumina grain which has silica grain, an EQC, or a degree of hardness beyond it as polishing grain, titanium oxide grain, zirconium-oxide grain, cerium-oxide grain, silicon-carbide grain, diamond grain, etc. are used, the same effect is acquired.

[0032] Moreover, in this example, although the case where BTA was used as a chemical agent was explained, using the glycine aqueous solution and the mixed solution of hydrogen peroxide solution as an etching agent, when the thing and ammonium nitrate which consist of oxidizers, such as an amidosulfuric acid or an aminoacetic acid, a mixed acid of an amidosulfuric acid, a hydrogen peroxide (H<sub>2</sub> O<sub>2</sub>) and a nitric acid, a hypochlorous acid, and ozone water, as an etching agent, an ammonium chloride, a chromic acid, etc. are used, the same effect is acquired. moreover, the reagent which forms this material and chelate compound, and a complex compound as a chemical agent according to the layer material which etches, for example, the various derivatives of BTA, the mixture containing these, thiourea, a thiourea derivative, a cupferron, the benzimidazole, a triazole, a salicylaldehyde, ethylenediamine, a cystine, a p-amino benzaldehyde, a halo acetic acid, a dodecyl mercaptan, and \*\*\*\*\* -- the same effect is acquired when monosaccharides, such as acids, a glucose, and a fructose, etc. are used Especially the various derivatives of BTA or BTA are effective when using the sulfuric-acid aqueous solution, the hydrochloric-acid aqueous solution, etc.

[0033] Moreover, in this example, although the polishing pad which consists of a resin sinking-in nonwoven fabric was used for the polishing pad, you may use the polishing pad which made nonwoven fabrics, such as polyester and a polyether, a firing polyurethane pad, or these two or more kinds of different pads rival that what is necessary is just what has a degree of hardness of the same grade. In addition, especially the thing that placed and changed the hydrogen fraction to the alkyl group etc. as a derivative of the various above-mentioned matter is desirable.

As an abrasive material, (Example 1 of a comparison) To the mixed solution (etching agent of Cu) of the 0.12 mols [l. ] glycine aqueous solution and 0.44 mols [l. ] hydrogen peroxide solution CMP was performed to the ground substrate 12 shown in drawing 2 (A) like an example except using what distributed silica grain (30nm of mean particle diameters) at 5.3 % of the weight as polishing grain, i.e., the thing which has not added BTA in the abrasive material which used it in the example.

[0034] Although the polishing speed was a part for about 250nm/and was high-speed as a result of CMP, compared with the case where a dishing value is an example, it was very large. That is, in 0.4 micrometer wiring width of face of a minimum line width,

the amount of dishings is about 300nm, and most Cus of Mizouchi for a wiring had disappeared in the wiring width of face of 5 micrometers or more. Moreover, when polishing time was extended further, all Cus in the slot for a wiring and puncturing for a connection wiring disappeared.

(Example 2) View 7 (A) is the cross section showing the ground substrate 12 used by this example. This ground substrate 12 is produced as follows. First, the silicon oxide 22 with a thickness of about 1 micrometer is formed on a silicon substrate 21. Subsequently, according to a usual photo-lithography process and a usual reactive-ion-etching process, patterning of the silicon oxide 22 is carried out, and the slot for a wiring with a width of face [ of 0.4-10 micrometers ] and a depth of 0.4 micrometers, puncturing for a connection wiring, etc. are formed in a silicon oxide 22. Subsequently, the titanium layer 31 with a thickness of about 20nm and the titanium-nitride layer 24 with a thickness of about 70nm are formed by the direct-current magnetron sputtering method on it, and the blanket W layer 32 with a thickness of about 600nm is succeedingly formed by the heat CVD using the mixed gas of 6 fluoride [ tungsten ] (WF<sub>6</sub>) gas and hydrogen gas. As shown in drawing 7 (A), the W layer 32 in front of CMP follows the level difference prepared in the silicon oxide 22 which is a base, and has the shape of a toothing.

[0035] Thus, CMP was performed using the polishing equipment to which the produced ground substrate 12 is shown in drawing 1, the slot for a wiring and the W layer [ surpluses / other than puncturing for a connection wiring ] 32 were removed, and an embedding wiring and W plug of W were formed. The abrasive material used for CMP makes the hydrogen-peroxide-solution solution of 5 volume % distribute alumina grain (50nm of mean particle diameters) at 1.0 % of the weight as polishing grain, and comes to add a 0.4 moreg [l. ] N-benzoyl-N-phenyl hydroxylamine (chemical agent). Moreover, polishing conditions are set to rotational frequency 100rpm of polishing pressure force 300gf/cm<sup>2</sup>, the turn table 14, and the vacuum-chuck electrode holder 11, and were made to become fixed about the temperature of a turn table at the room temperature of 25 degrees C.

[0036] As a result of CMP, the polishing speed was a part for about 300nm/, and was very high-speed. Moreover, in order to form W embedding wiring and W plug, you also have to remove the titanium layer 31 and the titanium-nitride layer 24 with the W layer 32. Since the polishing speed of the titanium layer 31 and the titanium-nitride layer 24 was a part for the almost same about 300nm/as the W layer 25, it was removable at high speed. Moreover, when W embedding wiring after CMP, W plug, and the exposed front face of a silicon oxide were observed by the scanning electron microscope, as shown in drawing 3, the blemish considered to have generated by CMP was not seen at all.

[0037] In addition, although to intermingle W, WO<sub>x</sub>, etc. is considered by W front face in CMP, which matter forms a chelate compound and BPA prepares a protective coat. Next, it investigated about the wiring width-of-face dependency of the amount of dishings. The result is shown in drawing 8. Here, the time of removing altogether the W layer 32, the titanium layer 31, and the titanium-nitride layer 24 of a heights was considered as the time of a polishing end. Wiring width of face was about 50nm in the wiring center section which is 10 micrometers, and the dishing value of W embedding wiring was a grade which is mostly satisfactory practically so that clearly from drawing 8. Moreover, even if it extends polishing time further, a dishing value understands that the protective coat formed on the W layer 32 is functioning effectively, when it takes having hardly increased into consideration.

[0038] In this example, although the case where W layer is used as a ground layer is explained, when a little impurity and a little alloying element contain in W, the same effect is acquired.

[0039] Furthermore, it is WF<sub>6</sub> although it explains as ground field in the above-mentioned example when forming W layer in the shape of a blanket. Gas and SiH<sub>4</sub> It is [ the mixed gas with gas, or ] H<sub>2</sub> to this mixed gas. this invention is applicable also to the case where the selective growth of W layer is performed using the gas which added gas. That is, when growing up W layer into tops, such as silicide layers, such as a silicon layer exposed at the base of the layer insulation layer which has a contact hole and a beer hall, for example, TiN layer, and TiSi, alternatively, it is possible to remove this W grain alternatively by collapse of selectivity, if the polishing technique of the above-mentioned example is used, although W grain may grow up to be an insulator layer front face.

[0040] Moreover, in this example, although the case where only alumina grain was used as polishing grain was explained, when the silica grain which has alumina grain, an EQC, or a degree of hardness beyond it as polishing grain, titanium oxide grain, zirconium-oxide grain, cerium-oxide grain, silicon-carbide grain, diamond grain, etc. are used, the same effect is acquired.

[0041] Moreover, in this example, although the case where BPA is used as a chemical agent is explained, using a hydrogen-peroxide-solution solution as an etching agent, when the iron nitrate aqueous solution, the mixed aqueous solution of a red potassium prussiate and ethylenediamine, the mixed aqueous solution of a red potassium prussiate and a phosphoric acid, etc. are used as an etching agent, the same effect is acquired. Moreover, the same effect is acquired when the reagent which forms this material and chelate compound, and a complex compound as a chemical agent according to the layer material which etches, for example, the various derivatives of BPA etc., is used.

[0042] Moreover, in this example, although the polishing pad which consists of a resin sinking-in nonwoven fabric was used for the polishing pad, you may use the polishing pad which made nonwoven fabrics, such as polyester and a polyether, a firing polyurethane pad, or these two or more kinds of different pads rival that what is necessary is just what has a degree of hardness of the same grade. In addition, especially the thing that placed and changed the hydrogen fraction to alkyl groups (a methyl group, ethyl group, etc.) as a derivative of the various above-mentioned matter is desirable.

(Example 2 of a comparison) CMP was performed to the ground substrate 12 shown in drawing 7 (A) as an abrasive material like [ the hydrogen-peroxide-solution solution of 5 volume % ] an example 2 except using what distributed alumina grain (50nm of mean particle diameters) at 1.0 % of the weight as polishing grain, i.e., the thing which has not added BPA in the abrasive material which used it in the example.

[0043] Although the polishing speed was a part for about 350nm/and was high-speed as a result of CMP, compared with the case where a dishing value is an example 2, it was very large. Namely, as shown in drawing 9, in 0.4 micrometer wiring width of face of a minimum line width, the amount of dishings was about 200nm, and along with the joint of W layer of the wiring center section formed at the time of heat CVD, etching advanced further, and it changed into the status that the hole 33 opened to the wiring.

(Example 3) In the polishing technique of this invention, the protective coat which becomes a metal, for example, the front face of Cu, from the compound (Cu-BTA) of a chemical agent, for example, BTA and a metal, is formed during polishing. In this case, when a protective coat is removed mechanically, it is etched in Cu by the etching component in an abrasive material. In this case, the activation energy  $E_{ae}$  of the etch rate of Cu is comparatively large, and the activity energy  $E_{ap}$  of the polishing speed of Cu is the parvus comparatively. This is because not only a chemical operation but a mechanical operation is included in polishing. Therefore, the relation of  $E_{ae} > E_{ap}$  is realized. For this reason, since, as for the value of the ratio of a polishing speed / etch rate, low temperature becomes large, the direction which performed CMP at low temperature from the viewpoint of a dishing reduction becomes advantageous.

[0044] Then, this example explains the case where CMP is performed at low temperature. When performing CMP less than at low temperature, for example, 20 degrees C, at least one of a turn table, a polishing pad, and abrasive materials may be cooled, first, the first phase may be ground at usual temperature (ordinary temperature), and the second phase may be continuously ground less than at low temperature, for example, 20 degrees C.

[0045] CMP was performed using the polishing equipment to which the ground substrate 12 shown in drawing 2 (A) is shown in drawing 1, the slot for a wiring and the Cu layer [ surpluses / other than puncturing for a connection wiring ] 25 were removed, and an embedding wiring and Cu plug of Cu were formed. The abrasive material used for CMP to the mixed solution (etching agent of Cu) of the 0.12 mols [l. ] glycine (C2 H5 O2 N) aqueous solution and 0.44 mols [l. ] hydrogen peroxide solution (H2 O2) Silica grain (30nm of mean particle diameters) is distributed at 5.3 % of the weight as polishing grain, and it comes to add a 0.001 more mols [l. ] benzotriazol (C6 H5 N3) (chemical agent). Moreover, polishing conditions were set to rotational frequency 60rpm of polishing pressure force 400gf/cm2, the turn table 14, and the vacuum-chuck electrode holder 11.

[0046] The temperature dependence of the polishing speed of Cu at this time and an etch rate was investigated. The result is shown in drawing 10. In addition, temperature is [ about ]. -It was made to change from 2 degrees C to about 100 degrees C. A polishing speed and an etch rate are exponential (exponent) of the inverse number (1/T) of temperature so that clearly from drawing 10. It was proportional. When the activation energy  $E_{ap}$  of a polishing speed and the activation energy  $E_{ae}$  of an etch rate were searched for from the inclination of these graphs, respectively,  $E_{ap}$  was about 0.7eV and  $E_{ae}$  was about 0.9eV. The inclination of each graph is negative, and since it is  $E_{ap} < E_{ae}$ , as for the value of the ratio of a polishing speed / etch rate, low temperature becomes large. Therefore, the amount of dishings of Cu wiring decreases so that the temperature of CMP is low temperature.

[0047] Next, it investigated about the wiring width-of-face dependency of each amount of dishings the case where set polishing temperature as the room temperature (24.0 degrees C), and CMP is performed, and at the time of setting polishing temperature as 14.0 degrees C, and performing CMP. The result is shown in drawing 11. Here, the time of removing altogether the Cu layer 25 and the titanium-nitride layer 24 on a heights was considered as the time of a polishing end. Wiring width of face was about 100nm in the wiring center section which is 10 micrometers, and the dishing value of Cu embedding wiring was a grade which is mostly satisfactory practically so that clearly from drawing 10.

[0048] Next, it investigated about the polishing time dependency of the amount with a wiring width of face [ the case where set polishing temperature as the room temperature (24.0 degrees C), and CMP is performed, and at the time of setting polishing temperature as 14.0 degrees C, and performing CMP ] of 5 micrometers of dishings. The result is shown in drawing 12. The increase in the amount of \*\*\*\*\*s at the time of an exaggerated polishing can be suppressed by performing CMP at low temperature so that clearly from drawing 12.

[0049] Moreover, when the front face of Cu embedding wiring after CMP and Cu plug was observed by the scanning electron microscope, as shown in drawing 2 (B), the blemish considered to have generated by CMP was not seen at all.

[0050] In this example, although the case where Cu layer is used as a ground layer is explained, when a little impurity and a little alloying element contain in Cu, or when layers, such as metals other than Cu, for example, Ag, aluminum, W, etc., and the layer which made these the principal component are used as a ground layer, the same effect is acquired.

[0051] Moreover, in this example, although the case where only silica grain was used as polishing grain was explained, when the alumina grain which has silica grain, an EQC, or a degree of hardness beyond it as polishing grain, titanium oxide grain, zirconium-oxide grain, cerium-oxide grain, silicon-carbide grain, diamond grain, etc. are used, the same effect is acquired.

[0052] Moreover, although the case where BTA is used as a chemical agent is explained in this example, using the glycine aqueous solution and the mixed solution of hydrogen peroxide solution as an etching agent As an etching agent, an amidosulfuric acid, or an aminoacetic acid and the mixed acid of an amidosulfuric acid, The same effect is acquired when the thing and ammonia which consist of oxidizers, such as a hydrogen peroxide (H2 O2), a nitric acid, a hypochlorous acid, and ozone water, an ammonium nitrate, an ammonium chloride, a chromic acid, etc. are used. moreover, the reagent which forms this material and chelate compound, and a complex compound as a chemical agent according to the layer material which etches, for example, the various derivatives of BTA, the mixture containing these, thiourea, a thiourea derivative, a cupferron, the benzimidazole, a triazole, a salicylaldoxime, ethylenediamine, a cystine, a p-amino benzaldehyde, a halo acetic acid, a dodecyl mercaptan, and \*\*\*\*\* -- the same effect is acquired when monosaccharides, such as acids, a glucose, and a fructose, etc. are used Especially

the various derivatives of BTA or BTA are effective when using the sulfuric-acid aqueous solution, the hydrochloric-acid aqueous solution, etc.

[0053] Moreover, in this example, although the polishing pad which consists of a resin sinking-in nonwoven fabric was used for the polishing pad, you may use the polishing pad which made nonwoven fabrics, such as polyester and a polyether, a firing polyurethane pad, or these two or more kinds of different pads rival that what is necessary is just what has a degree of hardness of the same grade. In addition, especially the thing that placed and changed the hydrogen fraction to the alkyl group etc. as a derivative of the various above-mentioned matter is desirable.

(Example 4) View 13 is the schematic diagram showing a part of polishing equipment used for the polishing technique of this invention. In this polishing equipment, the refrigerant circuit 41 is formed in the turn table 14. The temperature of the turn table 14 and the polishing pad 13 can be adjusted by carrying out conduction of the refrigerants, such as water and ethylene glycol, into this refrigerant circuit 41. The quality of the material of the main fractions of a turn table is glass fiber, and is small as compared with a metallic material, and since thermal conductivity is high, the quick temperature control is possible for it. [ of heat capacity ] It connects with two refrigerant cooling systems (condensators 42 and 43), and the refrigerant circuit 41 can change the circulation path of a refrigerant now at any time with the intermediate changeover switch 44. Furthermore, the abrasive-material supply systems 45 and 46 are connected to condensators 42 and 43, respectively, and the temperature of the abrasive material to supply can be adjusted now. Moreover, the jet nozzle 47 which sprays the cooled pure water on a turn table 14 is arranged in the upper part of a turn table 14.

[0054] CMP was performed using the polishing equipment which has the above-mentioned configuration by polishing of two phases, i.e., the first polishing, (room temperature polishing), and the second polishing (low-temperature polishing). In addition, by making setting temperature of a condensator 42 into 24.0 degrees C, and making setting temperature of a condensator 43 into 14.0 degrees C, the temperature control of the temperature of the abrasive material of the abrasive-material supply system 45 and its interior was carried out to 24.0 degrees C, and the temperature control of the temperature of the abrasive material of the abrasive-material supply system 46 and its interior was carried out to 14.0 degrees C. Moreover, the temperature control also of the temperature of the pure water of the jet-nozzle 47 interior was carried out to 14.0 degrees C.

[0055] First, the refrigerant circuit 41 of a turn table 14 was connected to the condensator 42 with the changeover switch 44, polishing temperature was set as 24.0 degrees C using the abrasive-material supply system 45, and CMP was performed like the example 3. Polishing time was made into about 80% of polishing end time at this time. Consequently, since polishing end time was 2 minutes and 37 seconds, the polishing time of the first polishing was 2 minutes and 5 seconds.

[0056] While the abrasive-material supply system 45 is stopped after the first polishing, the refrigerant circuit 41 of a turn table 14 is connected to a condensator 43 with a changeover switch 44 and 14.0-degree C cooling water was quickly circulated in the turn table 14, the turn table 14 was cooled by injecting the pure water cooled from the jet nozzle 47. When the temperature of polishing pad 13 front face on a turn table 14 became about 14 degrees C, using the abrasive-material supply system 46, polishing temperature was set as 14.0 degrees C, and CMP was performed like the example 3. By this second polishing, all the fractions that remained by the first polishing were ground. At this time, the polishing time of the second polishing was 2 minutes and 24 seconds.

[0057] Next, the wiring width-of-face dependency of the amount of dishings in ground Cu wiring was investigated. The result is shown in drawing 14. Also in CMP of two phases of a room temperature and low temperature, a dishing depressor effect of the same grade as CMP in low temperature is obtained so that clearly from drawing 14.

[0058]

[Effect of the Invention] The layer which consists of a material which makes a metal a principal component so that it may be filled up with the aforementioned concavity on the base which has a concavity on a front face according to the abrasive material and the polishing technique of this invention as explained above is formed. By the chemical machinery-polishing technique using the abrasive material containing the etching agent of the material which makes a principal component the chemical agent and the aforementioned metal which form a protective coat in the aforementioned layer front face by reacting with the material which makes the aforementioned metal a principal component the aforementioned layer -- grinding -- the inside of the aforementioned concavity -- a conductor -- since a layer is formed, while suppressing occurrence of a dishing or a blemish to the grade which is satisfactory practically -- a reliable conductor -- a layer can be formed at high speed

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[Translation done.]